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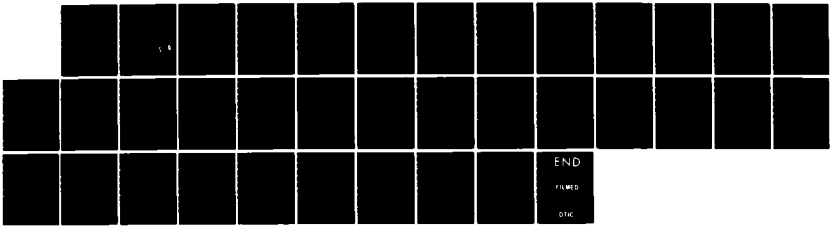

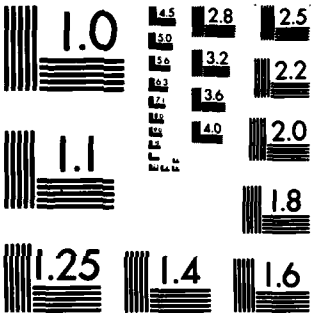

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Noncontinuum Solvent Effects Upon The Intrinsic Free-Energy Barrier For Electron-Transfer Reactions

by

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NONCONTINUUM SOLVENT EFFECTS UPON THE INTRINSIC FREE-ENERGY BARRIER FOR ELECTRON-TRANSFER REACTIONS

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Abstract

A phenomenological electrochemical approach is outlined by which "noncontinuum" contributions to the outer-shell intrinsic barrier to electron transfer, ΔG^*_{os}, resulting from specific reactant-solvent interactions can be estimated from the measured dependence of the formal potential upon the molecular and structural properties of the solvent. A simplified derivation, based on electrochemical half reactions, of the conventional dielectric continuum expression is given in order to clarify the physical origins of the outer-shell intrinsic barrier and to identify likely additional noncontinuum components. Numerical calculations for ammine and other redox couples involving specific ligand-solvent interactions indicate that the noncontinuum contributions to ΔG^*_{os} for both homogeneous and electrochemical exchange reactions can be surprisingly small (typically $\lesssim$ 1-2 kcal mol^{-1}) even when the thermodynamics of ion solvation are in severe disagreement with the dielectric continuum (Born) predictions. An additional noncontinuum component associated with vibrational distortions of outer-shell solvent may be significant for multicharged aquo complexes and other reactants engaging in strong ligand-solvent hydrogen bonding.

In recent years a number of theoretical approaches have been developed in order to describe the kinetics of outer-sphere electron-transfer processes.[1] It is useful to divide the overall free energy of activation into so-called "intrinsic" and "thermodynamic" contributions,[2] the former being the component that remains in the absence of the free-energy driving force ΔG°. Since evaluation of the latter component of the activation barrier is relatively straightforward given a knowledge of ΔG°, theoretical efforts have focussed attention on methods for calculating the former. These usually treat the intrinsic activation barrier in terms of separate contributions from the intramolecular reorganization of the reactant (inner-shell barrier) and the polarization of the surrounding noncoordinated solvent (outer-shell barrier). Treatment of the former has reached a high degree of sophistication, aided by the acquisition of accurate structural and vibrational data which enable the molecular distortions of the reactant to be calculated quantitatively for a number of reactions.[3] On the other hand, relatively little is known of the molecular structural details associated with outer-shell solvent reorganization. Consequently, this component is usually treated in terms of a model which regards the surrounding solvent as a dielectric continuum.[4]

Until recently, tests of these theoretical treatments were restricted chiefly to "relative rate" comparisons in a given solvent, usually water. These involve comparisons between the rate parameters of closely related reactions, especially between homogeneous self-exchange and cross reactions[5] and with corresponding electrochemical processes,[6] as well as the dependence of rates upon the thermodynamic driving force.[7] Unfortunately, the predicted form of such comparisons are insensitive to the model used for the outer- as well as the inner-shell barrier. Greater insight into the nature of the outer-shell barrier can be obtained by examining the kinetics of suitable homogeneous

self-exchange and electrochemical exchange reactions as a function of the solvent. A number of examinations of this type have been reported recently;[8-16] some indicate significant discrepancies with the solvent dependence predicted from the conventional dielectric continuum treatment.

The emergence of quantitative inner-shell structural data along with further theoretical developments has recently spawned several other confrontations between theory and experiment, involving the calculations of rate parameters for individual electron-transfer reactions ("absolute rate" comparisons). These involve scrunity of homogeneous cross reactions[17,18] and electrochemical processes[15,16,18] as well as homogeneous self-exchange reactions.[3,17,18,19] Although reasonable agreement between theory and experiment is obtained under some conditions[2,3,16,17] significant discrepancies occur in a number of cases.[3,15,18]

The theoretically derived rate constants are commonly larger than the experimental values.[3,15,18] One possible explanation is that the dielectric continuum model used in these calculations underestimates the solvent reorganization barrier. This notion would seem reasonable given that there is extensive evidence that electron transfer is often accompanied by large alterations in the short-range solvent structure, especially for multicharged transition-metal systems which can exhibit strong interactions between the coordinated ligands and the surrounding solvent.[20-23] However, discussions of the likely limitations of the dielectric continuum approach have often been confused by a lack of understanding of the physical origins of nonequilibrium solvent polarization.

We have recently outlined a modification to the dielectric continuum approach by which the intrinsic entropic barrier, ΔS^*_{int}, (i.e. the activation entropy that remains in the absence of an entropic driving force) can be calculated from thermodynamic data, thereby circumventing some features of the conventional

approach. This utilizes experimental entropy changes measured for the constituent electrochemical reaction(s) (i.e. the "reaction entropies", ΔS°_{rc} [20]). Larger and more structure-sensitive values of ΔS^{*}_{int} are obtained than using the conventional dielectric continuum formula.[24] In the present paper we describe a related approach by which the influence of short range reactant-solvent interactions (i.e. "noncontinuum electrostatic" interactions) upon the intrinsic free-energy barrier, ΔG^{*}_{int}, can be estimated from an analysis of electrochemical thermodynamic data. Besides clarifying the physical origins of solvation effects upon the intrinsic barrier, these considerations provide insight into the extent to which ΔG^{*}_{int} is likely to differ from the predictions of the conventional continuum model of ionic solvation.

Origin of the Outer-Shell Intrinsic Barrier

Before discussing noncontinuum effects it is useful to clarify the physical origin of the intrinsic free-energy barrier associated with outer-shell solvent reorganization, ΔG^{*}_{os}, on the basis of the dielectric continuum model. An enlightening mathematical derivation has been given by Marcus.[25] A simplified version of this analysis will first be summarized since it provides a useful framework for incorporating noncontinuum factors.

As for the corresponding treatment of intrinsic entropic barriers,[24] it is useful to consider the energetics of homogeneous electron-transfer processes in terms of a combination of the appropriate pair of electrochemical "half reactions" having the general form:

$$Ox + e^{-}(\phi_m) \rightleftharpoons Red \qquad (1)$$

where ϕ_m is the (Galvani) electrode-solution potential difference. For simplicity, we shall initially consider a single such electrochemical reaction in the so-called "weak overlap" limit, where the transition-state stability is unaffected by the presence of the electrode. This approach enables a simple physical picture to be provided of the activation process.[24]

According to the dielectric continuum treatment, the formation of the transition state involves a nonequilibrium solvent polarization process associated with random spatial fluctuations of nearby solvent molecules. This can usefully be perceived in terms of a hypothetical two-step charging process.[25] First, the charge of the reactant Ox is slowly adjusted to an appropriate value, usually about midway between that of the reactant and product, so that the solvent is polarized to an extent identical to that for the transition state (step 1). Then the charge is readjusted to that of the reactant sufficiently rapidly so that the solvent orientation remains unaltered (step 2), thereby yielding the nonequilibrium solvent polarization appropriate to the transition state.

In terms of the equilibrium dielectric continuum model due to Born, the change in free energy associated with charging (or discharging) spherical Ox to form Red in a given dielectric medium, $\Delta G^\circ_{rc,os}$, can be expressed as[26]

$$\Delta G^\circ_{rc,os} = \frac{(Z^2_{red} - Z^2_{ox})Ne^2}{2r\varepsilon_s} \qquad (2)$$

where Z_{red} and Z_{ox} are the ionic charge numbers of Ox and Red, N is the Avogadro number, e is the electronic charge, r is the reactant radius, and ε_s is the static dielectric constant of the surrounding solvent medium. Since step 1 involves slow (reversible) charging via a series of thermodynamic states, Eq. (2) can in principle also describe this process, yielding outer-shell

free energies, ΔG°_{os}, corresponding to a series of nonintegral charges between Z_{ox} and Z_{red}. Thus we can write

$$\Delta G^\circ_{os} = \frac{[(n + 1 - \alpha)^2 - (n + 1)^2]Ne^2}{2r\varepsilon_s} \qquad (3)$$

where n now represents the charge number in the reduced state, and α represents the fractional charge transferred, starting from the oxidized state having a charge number (n + 1). A resulting plot of the outer-shell free energy, ΔG°_{os}, against the effective ionic charge Z [=(n + 1) - α] is shown schematically in Fig. 1A (curve OSR, where O represents the oxidized and R the reduced species).

It is important to recognize that the overall intrinsic barrier for the electrochemical reaction (1) refers to a particular potential, ϕ°_m, (the "standard" or "formal" potential). At this point the difference in free energy between Ox and Red, ΔG°_{rc}, is cancelled by the electron free energy $F\phi^\circ_m$ (i.e. the energy gained by the transferring electron), so that the overall "electrochemical" free energy driving force, $\Delta \bar{G}^\circ_{rc}$, equals zero. A portion of this electron free energy, $F\phi^\circ_{m,os}$, can be considered to be associated with the outer-shell component of ΔG°_{rc}, $\Delta G^\circ_{rc,os}$, such that[27]

$$\Delta G^\circ_{rc,os} = -F\phi^\circ_{m,os} \qquad (4)$$

The changes in "chemical" free energy, ΔG°_{os}, anticipated from Eq. (3) during the step 1 charging process are therefore offset by corresponding changes in the electron free energy, $-\alpha F\phi^\circ_{m,os}$. However, compensation of these two components of $\Delta \bar{G}^\circ_{rc}$ will only be exact when α = 1 since the solvational and electrical portions are quadratically and linearly dependent, respectively, upon the ionic charge. Consequently the plot of the electrochemical free energy $\bar{G}^\circ_{rc,os}$ against the effective ionic charge, shown as curve OSR in Fig. 1B has a

symmetrical "bowed" shape. The magnitude of this nonlinearity, i.e. the vertical displacement of the OSR solid curve from the OR dashed straight line (Figs. 1A,B) depends on the extent of noncancellation of the opposing solvational and electronic contributions to the energetics of step 1. The resulting "static" contribution to the outer-shell intrinsic barrier, $\Delta G^{\circ}_{os,e}(stat)$, from Eqs. (3) and (4) can be expressed as:

$$\Delta G^{*}_{os,e}(stat) = \frac{(n + 1 - \alpha)^2 - (n + 1)^2}{n^2 - (n + 1)^2} \Delta G^{\circ}_{rc,os} - \alpha \Delta G^{\circ}_{rc,os} \qquad (5)$$

Inserting the Born expression for $\Delta G^{\circ}_{rc,os}$ [Eq. (2)] into Eq. (5) yields

$$\Delta G^{*}_{os,e}(stat) = -\alpha(1 - \alpha)(Ne^2/2r\varepsilon_s) \qquad (6)$$

Interestingly, neither the reactant or product charges appear in Eq. (6) so that the same intrinsic barrier would be expected irrespective of their magnitude or sign. Also note that $\Delta G^{*}_{os,e}(stat)$ is predicted from Eq. (6) to always be negative.

The contribution to $\Delta G^{*}_{os,e}$ arising from step 2 of the hypothetical charging process above can be derived by noting that an equivalent charging (or discharging) process is involved to step 1, only in the reverse direction and on a much more rapid time-scale than for reorganization of nuclear solvent coordinates. Under these conditions the solvent nuclei are fixed so that the dielectric properties are determined solely by internal electronic polarization, leading to the use of the optical dielectric constant, ε_{op}, rather than ε_s. This "optical" contribution to $\Delta G^{*}_{os,e}$, $\Delta G^{*}_{os,e}(op)$, will always increase the activation free energy since it refers to the formation of a nonequilibrium polarization state. The step 2 charging process is denoted by the vertical ST line in Figs. 1A and B.

Following the same procedure to that given above for the static component, we find that

$$\Delta G^*_{os,e}(op) = \alpha(1 - \alpha)(Ne^2/2r\epsilon_{op}) \qquad (7)$$

The free-energy profiles resulting from the sum of the contributions from steps 1 and 2, $\Delta G^*_{os,e}(stat) + \Delta G^*_{os,e}(op) = \Delta G^*_{os,e}$, are also shown in Figs. 1A and B. The curve OT is generated from a series of two-step charging processes for different values of α (such as the OS'T' route shown in Fig. 1A). The curve TR is the corresponding product curve, generated when the ionic charge in step 2 is instantaneously changed to that of the reduced (product) form rather than back to the reactant charge. The electrochemical free energy-charge dependence of these "reactant" and "product" curves (Fig. 1B) have the same slope, and intersect for $\alpha = 0.5$. Inserting $\alpha = 0.5$ into Eqs. (6) and (7) and adding them yields an expression for $\Delta G^*_{int,e}$:

$$\Delta G^*_{os,e} = \frac{Ne^2}{8r}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \qquad (8)$$

This is the dielectric continuum formula for the outer-shell intrinsic barrier for one-electron electrochemical reactions in the absence of reactant-electrode imaging interactions.[4] Including such imaging in terms of the distance, R_e, from the reactant to its image in the metal yields the well-known relation[4,25]

$$\Delta G^*_{os,e} = \frac{Ne^2}{8}\left(\frac{1}{r} - \frac{1}{R_e}\right)\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \qquad (9)$$

The corresponding expression for the intrinsic outer-shell barrier, ΔG^*_{os}, for homogeneous self-exchange reactions

$$Ox + Red \rightleftharpoons Red + Ox \qquad (10)$$

easily follows given that reaction (10) can be viewed as pair of coupled electrochemical reactions (1), yielding twice the overall intrinsic barrier.[24]

Taking into account the decrease in solvent polarization resulting from the finite distance between the homogeneous reaction centers, R_h, yields the familiar expression[4] for the homogeneous outer-shell intrinsic barrier:

$$\Delta G^*_{os} = \frac{Ne^2}{4}\left(\frac{1}{r} - \frac{1}{R_h}\right)\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \qquad (11)$$

Incorporating Noncontinuum Factors

Although the foregoing is concerned only with electron transfer within the framework of the conventional dielectric continuum model, the discussion leading to Eqs. (8), (9) and (11) suggests a simple means of generalizing the analysis to include noncontinuum factors. It is evident that the static component of the intrinsic solvent barrier, $\Delta G^*_{os,e}(stat)$, is linked closely to the Born estimate of $\Delta G^\circ_{rc,os}$ [Eq. (2)], and particularly to the accompanying quadratic dependence of free energy upon ionic charge. Given the well-known severe deficiencies of the Born model for estimating the energetics of ion solvation, it seems preferable to employ instead estimates of $\Delta G^\circ_{rc,os}$ derived from more sophisticated models, or best of all, from experimental thermodynamic data. All that is necessary is to establish the magnitude of $\Delta G^\circ_{rc,os}$ and its functional dependence upon ionic charge. To the extent that such parameters are interpretable in terms of specific molecular interactions, the influence of such interactions upon the intrinsic outer-shell barrier can thereby be predicted.

For the sake of simplicity, we will first assume that the component of the outer-shell free energy arising from noncontinuum factors also depends quadratically upon the net ionic charge (*vide infra*). Figure 2 contains schematic G°_{os} - Z curves designed to illustrate the influence of such specific reactant-solvent interactions upon $\Delta G^*_{os,e}(stat)$ for a cationic redox couple (i.e. where $n \geq 0$). Figure 2A represents the schematic G°_{os} - Z curve expected on the basis of Eq. (3). Note that the oxidized state, having the higher ionic charge (n+1),

has a more positive outer-shell free energy than the reduced state. This follows on the basis of the continuum model from the imperfect screening of the ionic charge by the surrounding dielectric for finite values of ε_s.[26]

Figure 2B represents a schematic G°_{os} - Z curve anticipated as a consequence of charge-dependent specific reactant-solvent interactions. In contrast to Fig. 2A, the outer-shell free energy of Ox is now depicted to lie *below* that for Red. This is expected since the greater ionic charge of Ox will engender stronger reactant-solvent interactions, leading to a lower free energy, than that for Red. Providing that this additional noncontinuum component of the outer-shell free energy change, $\Delta G^{\circ\prime}_{rc,os}$, is quadratically (or at least nonlinearly) dependent upon the ionic charge, then the "bowing" of the $G^{\circ\prime}_{os}$ - Z curve (O'T'R') shown in Fig. 2B will always yield a *positive* component of $\Delta G^*_{os,e}$(stat), contrasting the *negative* continuum term [Eq. (6)]. As for the continuum case, the noncontinuum component of $\Delta G^*_{os,e}$(stat) will equal the vertical difference (A'T') between the solid bowed curve and the dashed straight line between Ox and Red at the appropriate value of α, as indicated in Fig. 2B. Clearly, the magnitude of $\Delta G^*_{os,e}$(stat) will increase as $\Delta G^{\circ\prime}_{rc,os}$ increases.

Generally, then, we may write

$$\Delta G^*_{os,e}(\text{stat}) = f[\Delta G^\circ_{rc,os}(\text{cont})] + f(\Delta G^{\circ\prime}_{rc,os}) \qquad (12)$$

where the first and second terms on the right-hand side are suitable functions of the solvational energy changes associated with the continuum and noncontinuum components, respectively, of $\Delta G^*_{os,e}$(stat). Assuming that the former is given by Eq. (6) and the latter has the same form as in Eq. (5), if $\alpha = 0.5$ we can write

$$\Delta G^*_{os,e}(\text{stat}) = \frac{Ne^2}{8r\varepsilon_s} + \left[\frac{(n+0.5)^2 - (n+1)^2}{n^2 - (n+1)^2} - 0.5\right]\Delta G^{\circ\prime}_{rc,os}$$

$$= -Ne^2/8r\varepsilon_s + \Delta G^{\circ\prime}_{rc,os}/(8n+4) \qquad (13)$$

If the optical component, $\Delta G^{*}_{os,e}(op)$, [Eq. (7)] is included along with imaging interactions as before (*vide infra*), a more general expression for the outer-shell intrinsic barrier results:

$$\Delta G^{*}_{os,e} = \frac{Ne^2}{8}\left(\frac{1}{r} - \frac{1}{R_e}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) + \Delta G^{\circ\prime}_{rc,os}/(8n + 4) \qquad (14)$$

The imaging correction is omitted from the noncontinuum term since the likely short-range nature of the latter should make it insensitive to the proximity of the image charge.

As for the continuum treatment above, Eq. (14) can be adapted to yield the corresponding relation for the outer-shell intrinsic barrier for homogeneous reactions:

$$\Delta G^{*}_{os} = \frac{Ne^2}{4}\left(\frac{1}{r} - \frac{1}{R_h}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) + \Delta G^{\circ\prime}_{rc,os}/(4n + 2) \qquad (15)$$

Equations (14) and (15) have a similar form to those derived from a corresponding treatment for the intrinsic activation entropy, ΔS^{*}_{int} [Eq. (14) of ref. 24]. They provide a simple means of correcting the static portion of the intrinsic solvent barrier for the likely severe deficiencies of the Born model.

Experimental Estimates of $\Delta G^{\circ\prime}_{rc}$

The estimation of outer-shell intrinsic barriers using Eqs. (14) and (15) clearly depends upon the acquisition of at least approximate estimates of the noncontinuum term $\Delta G^{\circ\prime}_{rc,os}$. Since this quantity is a difference in free energy for ions of different charges, values cannot be obtained without resort to some extra-thermodynamic assumption. The entropic component of this free-energy difference between Red and Ox (the "reaction entropy" ΔS°_{rc}) can be determined reliably from the temperature dependence of the formal potential, E_f, using a nonisothermal cell arrangement.[20] This is because the temperature dependence of

E_f under these conditions approximates closely to the quantity $(d\varphi^\circ_m/dT)$ required to evaluate ΔS°_{rc}.

The evaluation of $\Delta G^\circ_{rc,os}$ values is less straightforward because *absolute* Galvani potentials, rather than their temperature derivatives, are required [Eq. (4)]. Nevertheless, *relative* values of $\Delta G^{\circ\prime}_{rc,os}$ for different solvents, $\Delta(\Delta G^{\circ\prime}_{rc,os})$, can be obtained approximately from the corresponding difference in formal potential, $-F(E'_f - E''_f)$.[22] This requires that the formal potentials be evaluated, or estimated, with respect to a reference electrode having a solvent-independent Galvani potential. Although an extrathermodynamic assumption is necessarily involved, such potential scales can be established in different solvents using, for example, the "Tetraphenylarsonium-Tetraphenylborate" (TATB) assumption. This enables approximate values of $\Delta(\Delta G^{\circ\prime}_{rc,os})$ to be determined from formal potential data.[22]

Although such an approach does not yield the required absolute values of $\Delta G^{\circ\prime}_{rc,os}$, approximate estimates can nonetheless be obtained using a related procedure. This involves plotting E_f for the redox couple of interest on a suitable reference scale in a series of solvents against an empirical solvent parameter that provides a measure of the anticipated reactant-solvent interactions. Providing that a reasonable correlation is obtained, absolute estimates of $\Delta G^{\circ\prime}_{rc,os}$ in a given solvent can be obtained from the difference between E_f in that solvent and the value measured in (or extrapolated to) a solvent environment where such specific interactions are essentially absent.

Redox couples containing ammine and related ligands, such as $Ru(NH_3)_6^{3+/2+}$ and $Co(en)_3^{3+/2+}$ [en = ethylenediamine], systems with which to illustrate this procedure. These couples have been shown to engage in strong solvent-ligand donor-acceptor interactions with the ammine hydrogens acting as electron acceptors.[22,28] These interactions are stronger in the oxidized state due to the larger positive charge on the ammine hydrogens, leading to increasingly

negative values of E_f, and hence larger values of $\Delta G^{\circ\prime}_{rc,os}$, as the donating properties of the solvent increase.[22] A plot of the formal potential for $Ru(NH_3)_6^{3+/2+}$ with respect to that for the ferricinium-ferrocene (Fc^+/Fc) couple, E_f^{Fc}, in a number of solvents against the solvent "donor number", DN, is given in Fig. 3 (line 4). These data were taken from ref. 22. The Fc^+/Fc couple provides a suitable "reference reaction" with which to examine the solvent dependence of E_f associated with ligand acceptor properties. Thus although the electrode potential of this couple does exhibit a mild solvent dependence on the TATB scale,[22] this arises predominantly from an entropic component[29] which evidently is associated with disruption of the internal solvent structure.[23] The intercept of this plot, i.e. the value of E_f^{Fc} where DN = 0, should correspond to the absence of ligand-solvent donor interactions. Thus approximately

$$\Delta G^{\circ\prime}_{rc,os} = -F[E_f^{Fc} - E_f^{Fc}(DN = 0)] \qquad (16)$$

This relationship yields values of $\Delta G^{\circ\prime}_{rc,os}$ for $Ru(NH_3)_6^{3+/2+}$, and similarly for other ammine and related couples[22] that are substantially larger than the Born values obtained from Eq. (2) in solvents that exhibit moderate or strong electron-donating capability. Besides $Ru(NH_3)_6^{3+/2+}$, representative data for $Co(en)_3^{3+/2+}$ (en = ethylenediamine) are also plotted in Fig. 3 (line 5). From Fig. 3, $\Delta G^{\circ\prime}_{rc,os} \simeq 13$ kcal mol^{-1} for $Ru(NH_3)_6^{3+/2+}$ in water (DN = 18), whereas from the continuum model [Eq. (2)], $\Delta G^{\circ}_{rc,os} = -3.0$ kcal mol^{-1} for r = 3.5 Å.[22] Insertion of $\Delta G^{\circ\prime}_{rc,os} = 13$ kcal mol^{-1} into Eq. (15), given that n = 2 for $Ru(NH_3)_6^{3+/2+}$, yields $\Delta G^{*}_{os} = 7.8$ kcal mol^{-1} for r = 3.5 Å and R_h = 7 Å. The conventional continuum treatment [Eq. (11)] yields $\Delta G^{*}_{os} = 6.5$ kcal mol^{-1}. The additional noncontinuum term in Eq. (15) therefore constitutes a small yet significant (1.3 kcal mol^{-1}) component of ΔG^{*}_{os}.

For comparison, Fig. 3 (line 1) shows corresponding data for $Fe(bpy)_3^{3+/2+}$ [bpy = 2,2'-bipyridine], again taken from ref. 22. This system is an example of a couple that engages in relatively nonspecific ligand-solvent interactions since coordinated 2,2'-bipyridine does not contain any polar groups anticipated to interact specifically with the surrounding solvent. As expected the E_f^{Fc}-DN plot has a slope close to zero, so that $\Delta G^\circ_{rc,os} \sim 0$ even in strongly donating solvents such as dimethylsulfoxide and N,N-dimethylformamide. The same behavior is also seen for other polypridine couples, such as $Ru(bpy)_3^{3+/2+}$, $Cr(bpy)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Fe(phen)_3^{3+/2+}$ [phen = 1,10-Phenanthroline].[22] Noncontinuum factors are therefore unlikely to contribute significantly to the intrinsic outer-shell barrier for these couples. Plots of E_f^{Fc} against solvent DN for two mixed ammine-bipyridine couples, $c\text{-}Ru(NH_3)_2(bpy)_2^{3+/2+}$ and $Ru(NH_3)_4bpy^{3+/2+}$, are also shown in Fig. 3 (lines 2 and 3).[32] Note that the slopes of these plots are intermediate between those for $Fe(bpy)_3^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$. Indeed the E_f^{Fc}-DN slopes (the "Solvent Donor Selectivity") are approximately proportional to the number of ammine ligands, suggesting that each ligand provides an independent additive contribution to the overall solute-solvent interactions.

Several other types of noncontinuum contributions to the static component of ΔG^*_{os} may also be anticipated. Thus reactants containing donating groups, such as complexes having chiefly anionic ligands and radical anions with electronegative centers, may interact specifically with solvents which can act as strong electron acceptors. For example a correlation, analogous to that in Fig. 3, has been observed between the formal potential for $Fe(CN)_6^{3-/4-}$ and the electron-accepting ability of the solvent as measured by the "acceptor number".[30]

It is important to recognize that such specific reactant-solvent interactions are only anticipated to influence the reaction energetics when the extent of

such interactions differ between Ox and Red. The form of Eqs. (14) and (15) indicate that the influence of these specific interactions will always *increase* the intrinsic barrier provided that they are greater for the redox state carrying the larger net charge. The applicability of these relations is also dependent on the occurrence of a quadratic relation between the free energy and the net ionic charge (*vide infra*).

Comparisons With Experiment

The inclusion of noncontinuum contributions to the outer-shell intrinsic barrier as in Eqs. (14) and (15) provide corrections to the conventional treatment that can at least qualitatively account for some of the apparent discrepancies seen with solvent-dependent kinetic data.[12-15] However, a difficulty of testing such theoretical predictions with rate data is that a number of factors besides the outer-shell barrier can dominate the observed solvent dependence, such as uncertainties in work term corrections,[15,18] nonadiabaticity, and solvent dynamical effects upon the preexponential factor.[16] Further examination of this matter will be considered elsewhere.

A more direct test of models for the solvent intrinsic barrier is provided by solvent-dependent studies of photoinduced electron transfer within symmetrical binuclear complexes in homogeneous solution. This is because the reorganization energy is directly probed via the intervalence spectral transition energy, rather than indirectly via reaction rates.[31b]

The intramolecular electron-transfer system $[(NH_3)_5Ru^{III}$(4,4'-bipyridine)$Ru^{II}(NH_3)_5]^{5+}$ studied in several solvents by Creutz[31] is particularly germane to the present discussion since significant noncontinuum contributions to ΔG^*_{os} arising from ammine ligand-solvent interactions would be expected on the basis of Eq. (15).

Table I contains a comparison between the experimental and theoretical intrinsic barriers for this system in five solvents of varying donicity. The experimental outer-shell barriers, $\Delta G^*_{os}(exp)$, were obtained from the experimental optical reorganization energies, λ_{exp}, by subtracting the inner-shell component calculated from structural data to yield the outer-shell component, λ_{os}, and noting that $\Delta G^*_{os} = \lambda_{os}/4$.[31] The continuum estimates, $\Delta G^*_{os}(cont)$, were obtained by taking $r = 4.0$ Å, $R_h = 8$ Å in Eq. (11) as noted in ref. 31a. The corresponding noncontinuum-corrected estimates, $\Delta G^*_{os}(Eq\ 15)$, were obtained by evaluating the additional noncontinuum term in Eq. (15). The appropriate values of $\Delta G^{\circ\prime}_{rc,os}$ were obtained from Eq. (16) by assuming that the plot of E_f^{Fc} vs DN for the $Ru(NH_3)_5^{3+/2+}$ moiety is 25 mV per DN unit; (estimated by interpolation from the data for the $Ru(NH_3)_4bpy^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples in Fig. 3).

The last two columns in Table I report the differences between the values of $\Delta G^*_{os}(exp)$ and the corresponding theoretical quantities derived from the continuum and noncontinuum-corrected treatments. As anticipated from Eq. (15), the former [Eq. (11)] does slightly underestimate the magnitude of $\Delta G^*_{os}(exp)$ for solvents of higher DN (e.g. DMF, DMSO). However, the noncontinuum component in Eq. (16) apparently *overestimates* this correction by ca. 3-5 fold, so that $\Delta G^*_{os}(exp) < \Delta G^*_{os}(Eq\ 15)$. The simple continuum treatment therefore yields values of ΔG^*_{os} that are numerically closer to $\Delta G^*_{os}(exp)$ than are those obtained with inclusion of the noncontinuum component. This result might be taken as evidence against the validity of the noncontinuum correction itself. It is more likely, however, that the close correspondence between $\Delta G^*_{os}(exp)$ and $\Delta G^*_{os}(cont)$ is somewhat fortuitous, especially given the uncertainties as to the exact applicability of the simple "two-sphere" model embodied in both Eqs. (11) and (15) to systems of differing geometries.[4b] Thus several modifications to Eq. (11) that take into account interactions between the reacting cospheres yield somewhat (10-30%) smaller values of $\Delta G^*_{os}(cont)$. Inclusion of the additional noncontinuum component as in Eq. (15)

to such relations yields estimates of ΔG^*_{os} that are closer to $\Delta G^*_{os}(exp)$ than are obtained in its absence.

Discussion

The foregoing demonstrates that short-range reactant-solvent interactions can constitute only a small ($\lesssim$ 1-2 kcal mol^{-1}) component of the outer-shell intrinsic barrier even in the face of a large or even predominant influence of such factors upon the redox thermodynamics. Moreover, the data in Table I suggest that the noncontinuum effect may be even smaller than that expected from Eqs. (14) and (15).

The quantitative validity of these relations rests primarily on the correctness of the assumed quadratic dependence of $\Delta G^{\circ\prime}_{rc,os}$ upon the net ionic charge. The quadratic dependence of the continuum portion, $\Delta G^{\circ}_{rc,os}$, assumed in deriving these relations, is predicted from a statistical-mechanical treatment based on ion-solvent and solvent-solvent multipole interactions.[34,35] However, this seems less likely to be entirely correct for the noncontinuum component, $\Delta G^{\circ\prime}_{rc,os}$, associated with specific ligand-solvent interactions. These can be viewed as individual charge-dipole interactions, the charge residing on the ligand acceptor (or donor) site and varying with the oxidation state. Such charge-dipole interactions vary *linearly* with the charge,[36] the quadratic component for ion-solvent interactions being associated instead with the mutual interaction of dipoles between solvent molecules.[34] Moreover, variations in the central ionic charge are anticipated to yield proportionately smaller changes in the effective charge on the ligands[37] thereby providing more linear variations of $\Delta G^{\circ\prime}_{rc,os}$ with ionic charge. Unfortunately, no direct experimental information is available. Some support to this expectation is nevertheless provided by the very similar variations in E_f^{Fc} observed for $Ru(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_5NCS^{2+/+}$ with solvent DN.[23,39] Therefore $\Delta G^{\circ\prime}_{rc,os}$ might be expected to vary with charge in a manner intermediate between linear and quadratic. Since the noncontinuum contribution to ΔG^{*}_{os} will entirely disappear in the former case, one might expect that Eqs. (14) and (15), obtained by assuming the latter case, provide *upper limits* to the magnitude of this effect.

It is therefore concluded that even extensive changes in short-range reactant-solvent interactions may yield only small and even negligible influences upon the outer-shell intrinsic barrier. This is not to say that such interactions

do not strongly affect the reaction energetics, but rather that this influence is largely accounted for by the driving force component of the free-energy barrier so that it has little effect upon the intrinsic portion. It is important to note that contemporary electron-transfer theories are largely concerned with calculating ΔG^*_{int} and the *dependence* of the activation barrier upon the driving force. The reaction thermodynamics, upon which the primary influence of solvent noncontinuum factors are felt, are not addressed by these theories, their evaluation being left entirely to experiment.

Other Limitations of the Continuum Treatment

It is also of importance to examine if the validity of the continuum component of Eqs. (14) and (15), contained in the first term on the right-hand side of these relationships, is itself liable to be influenced by short-range reactant-solvent interactions. It might be anticipated that smaller values of ε_s than the normal bulk values would be appropriate in Eqs. (14) and (15), especially for multicharged ions, due to partial dielectric saturation in the vicinity of the reactant. Although small effective values of ε_s are deduced for solvent molecules in the primary solvation shell, values that approach that for the bulk medium are estimated for the secondary and subsequent shells,[40] i.e., the "outer shell" considered here. In any case, since typically $\varepsilon_{op} \geq 20\varepsilon_s$ this static component should yield only a relatively small ($\leq 5\%$) contribution to ΔG^*_{os}. Especially small effective values of ε_s in the outer shell might be anticipated for reactants that strongly orient surrounding solvent molecules by means of specific donor-acceptor interactions. However, since this effect is predicted to decrease ΔG^*_{os} [Eq. 15)], it should tend to be offset by the small corresponding increase in ΔG^*_{os} anticipated from the noncontinuum term.

It remains to consider possible noncontinuum effects upon the optical component of ΔG^*_{os}, as expressed in Eq. (7). Since ε_{op} is typically small (ca. 1.5 - 2) the optical component commonly provides a large, probably

predominant, contribution to ΔG^*_{os}. Similarly to ϵ_s, the appropriate value of ϵ_{op} to use in Eqs. (14) and (15) is an appropriately weighted "local" quantity representative of nearby solvent molecules. This might be anticipated to differ from the bulk ϵ_{op} value, at least with reactants featuring extensive short-range solvent polarization. However, ϵ_{op} is expected to be insensitive to the intermolecular solvent structure since it reflects only the electronic polarizability of the solvent molecules. Moreover, the relatively small ϵ_{op} values indicate that the "screening" ability of the nonequilibrium polarization by surrounding solvent molecules is relatively ineffective; this polarization should therefore extend over relatively large distances from the reactant center where ϵ_{op} should closely approximate the average bulk value. At least for water molecules, the anisotropy of the electronic polarizability (and hence of ϵ_{op}) is small[41] so that even extensive short-range solvent orientation should have little influence on the effective value of ϵ_{op} in Eqs. (14) and (15). Nevertheless, significant variations in ϵ_{op} in the vicinity of solvents can be anticipated for more asymmetric solvents, especially those that are strongly oriented by the reactant.

In a recent polemical article, Khan and Bockris[42] have suggested another possible source of noncontinuum effects for strongly hydrated ions associated with "inner-shell" like distortions of water molecules in the secondary solvation shell. Such a contribution can be considered in terms of the average alteration in hydrogen-bond distances beween the coordination shell of aquo (or possibly other hydrogen-bonding) ligands and adjacent water molecules brought about by electron transfer. The magnitude of this contribution to ΔG^*_{int}, $\Delta G^*_{os}(O\cdots H)$, can in principle be determined from the conventional expression[1e]

$$\Delta G^*_{int} = 0.5 n f_i (\Delta a/2)^2 \qquad (17)$$

where Δa is the equilibrium bond-distance change brought about by electron transfer, f_i is the reduced force constant of the ith bond, and n is the number of bonds undergoing distortion. A rough estimate of Δa for $M(OH_2)_6^{3+/2+}$ couples is provided by the ca. 0.1 Å difference in the O···H hydrogen bond distance between primary and secondary hydration for M^{3+} versus M^{2+} crystalline hydrates.[43] A force constant of ca. 3×10^4 dyne cm is estimated for such hydrogen bonds from spectral data,[44] which for n = 6, yields $\Delta G^*_{os}(O\cdots H) \sim 1$ kcal mol^{-1}. Although only a very rough estimate, this demonstrates that such distortions of secondary shell solvation may provide a significant additional contribution to ΔG^*_{int} for strongly hydrogen-bonded systems. Such a contribution may account in part for the surprisingly large solvent deuterium isotope effects observed for both electrochemical and homogeneous exchange of metal aquo complexes.[46-8] Thus the slightly stronger hydrogen-bonding properties anticipated for the deuterated ligands[49] may yield a larger average value of n and hence of $\Delta G^*_{os}(O\cdots H)$ in Eq. (20).

This "microscopic" approach to estimating components of ΔG^*_{os} associated with specific reactant-solvent interactions is quite distinct from, yet complimentary to, the phenomenological approach embodied in Eqs. (14) and (15). It is important to recognize that such vibrational distortion, similarly to the "optical" component of the hypothetical two-step charging process, will contribute to ΔG^*_{os} *irrespective* of the functional form of the free energy-reaction coordinate profile associated with these processes. In contrast, the "static" component of ΔG^*_{os} is associated only with the nonlinear portion of the free-energy charging curve for this process. This is because the former describe components of ΔG^*_{os} associated with *nonequilibrium* solvent polarization which are necessarily absent in the reactant and product states.

Concluding Remarks

Along with the related examination of specific reactant-solvent effects upon the intrinsic entropic barrier,[24] the present phenomenological treatment further demonstrates the virtues of employing electrochemical thermodynamic data to yield insight into the role of reactant-solvent interactions upon the kinetics of electron-transfer reactions. The results indicate that such interactions may typically yield only a surprisingly small contribution to the intrinsic barrier. The well-documented severe limitations of the Born and other continuum models for estimating the thermodynamics of ionic solvation[34,36] are demonstrated to exert surprisingly little influence upon the solvation component of the intrinsic barrier. Nevertheless, noncontinuum effects may contribute more significantly to ΔG^{*}_{os} for systems that involve vibrational distortions of outer-shell solvent molecules. Especially in this regard, the formulation of molecularly based theoretical models for the ouer-shell reorganization process[50] should be most revealing.

Acknowledgments

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(27) The overall magnitude of ΔG°_{rc} is determined by an inner-shell component as well as the outer-shell term, $\Delta G^\circ_{rc,os}$, considered here. The former arises from the differences in electronic structure between Ox and Red associated with ligand-field stabilization, etc., and is considered to be unaffected by the ion-solvent interactions.

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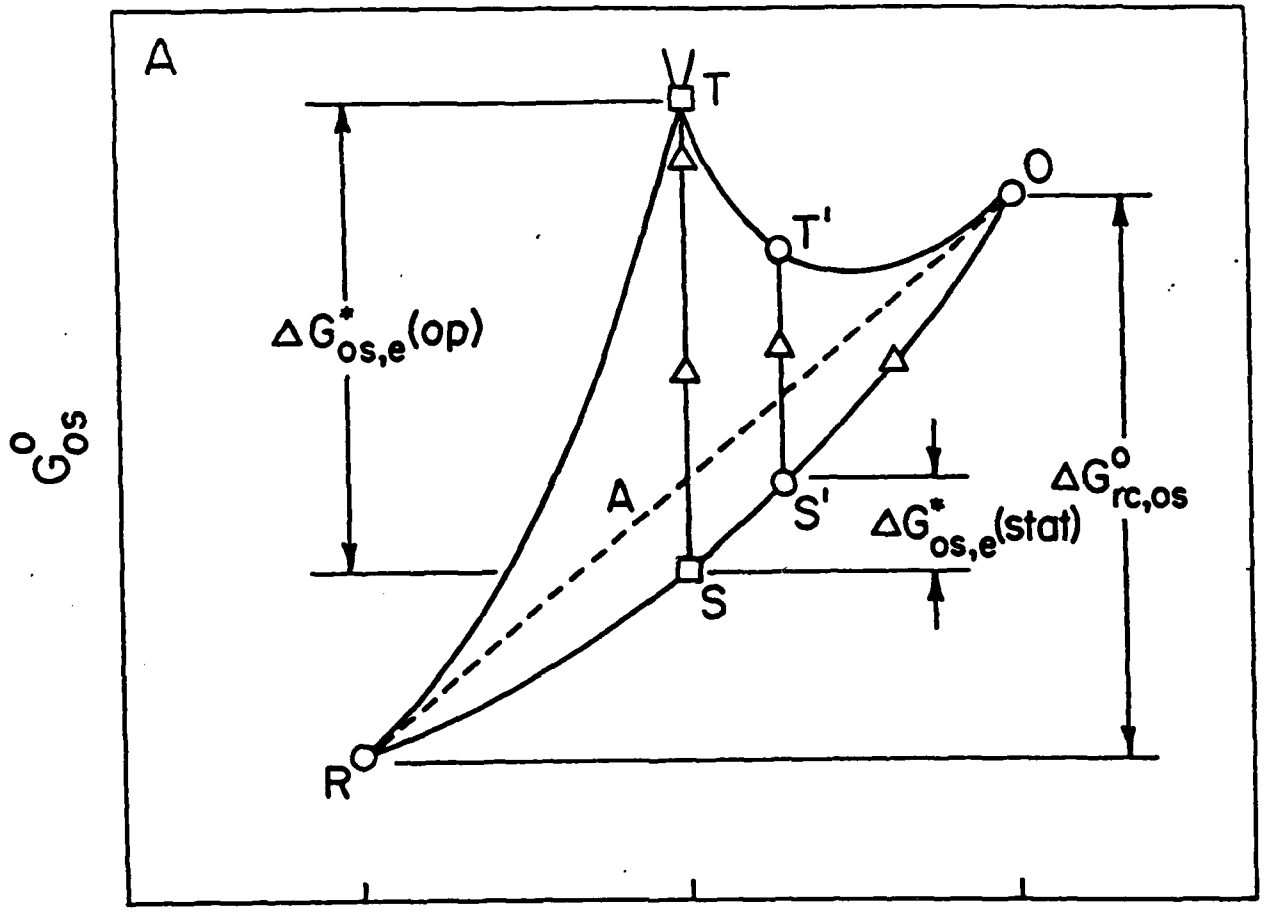
TABLE I Noncontinuum Contributions to Optical Electron-Transfer Barrier (kcal mol^{-1}) for $(NH_3)_5Ru^{III}$(4,4'-bipyridine)$Ru^{II}(NH_3)_5$

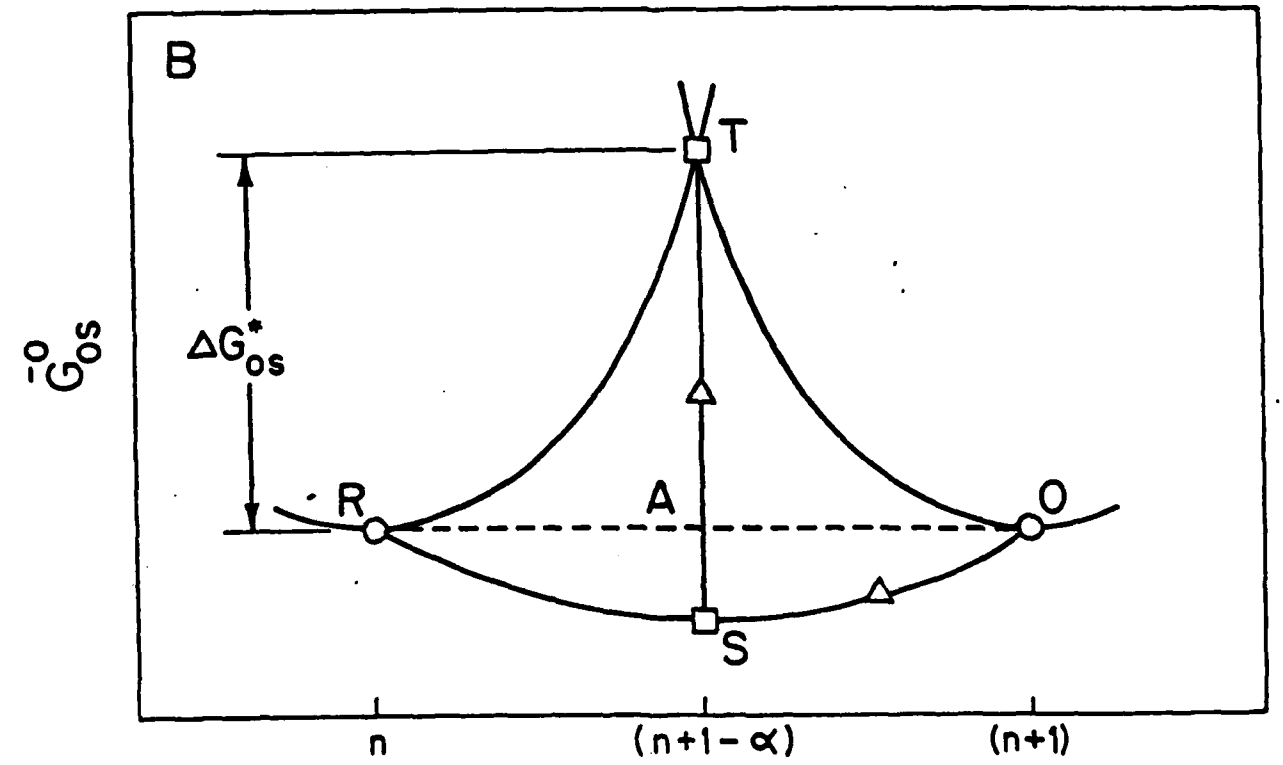
Solvent	ΔG^*_{os}(exp)[a] (1)	ΔG^*_{os}(cont)[b] (2)	ΔG^*_{os}(Eq 15)[c] (3)	(1)-(2)	(1)-(3)
D_2O	6.80	6.65	7.77	0.15	-0.97
Methanol	6.46	6.46	7.52	0	-1.06
Acetonitrile	6.33	6.36	7.30	-0.03	-0.97
DMF	6.13	5.71	7.36	0.42	-1.23
DMSO	5.78	5.45	7.30	0.33	-1.52

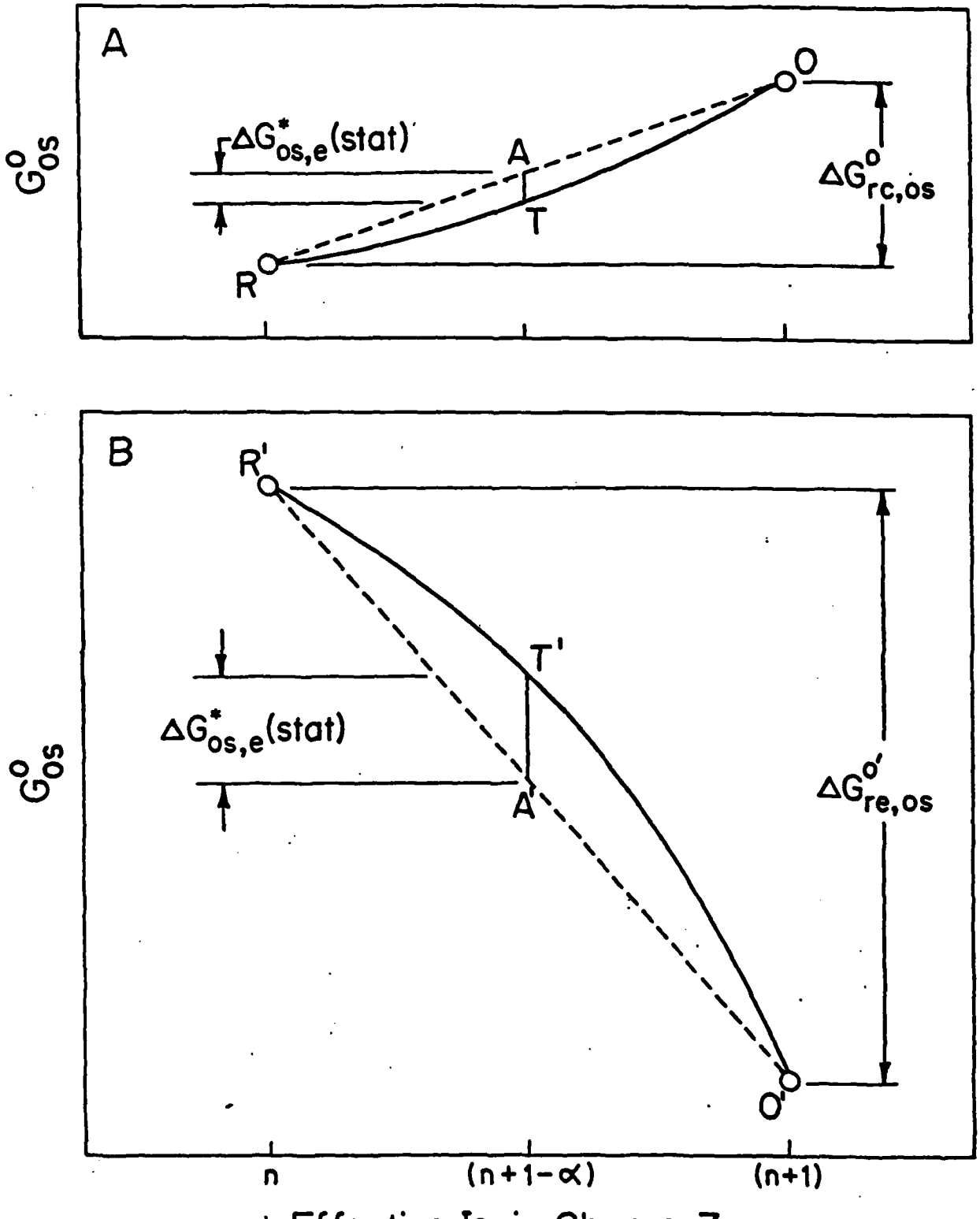
[a] Intrinsic outer-shell barrier (kcal mol^{-1}) for reaction in solvent listed, extracted from optical absorption data in ref. 31a as outlined in the text.

[b] Intrinsic outer-shell barrier (kcal mol^{-1}) as estimated from dielectric continuum model [Eq. (11)] with r = 4.0 Å, R_h = 8.0 Å (see ref. 31a).

[c] Intrinsic outer-shell barrier (kcal mol^{-1}) as estimated from Eq. (15). Continuum component calculated as in footnote (b); values of $\Delta G^{\circ\prime}_{rc,os}$ for noncontinuum term estimated from data in Fig. 3 using Eq. (16) as noted in text.


A
T
T'
O
$\Delta G^{*}_{os,e}(op)$
G^{o}_{os}
A
S'
$\Delta G^{*}_{os,e}(stat)$
$\Delta G^{o}_{rc,os}$
S
R


B
T
ΔG^{*}_{os}
G^{o}_{os}
R
A
O
S
n
(n+1−α)
(n+1)
Effective Ionic Charge, Z


A
G^o_{os}
$\Delta G^*_{os,e}$(stat)
A
T
O
R
$\Delta G^o_{rc,os}$
B
G^o_{os}
R'
T'
A'
O'
$\Delta G^*_{os,e}$(stat)
$\Delta G^{o'}_{re,os}$
n
(n+1−α)
(n+1)
Effective Ionic Charge, Z

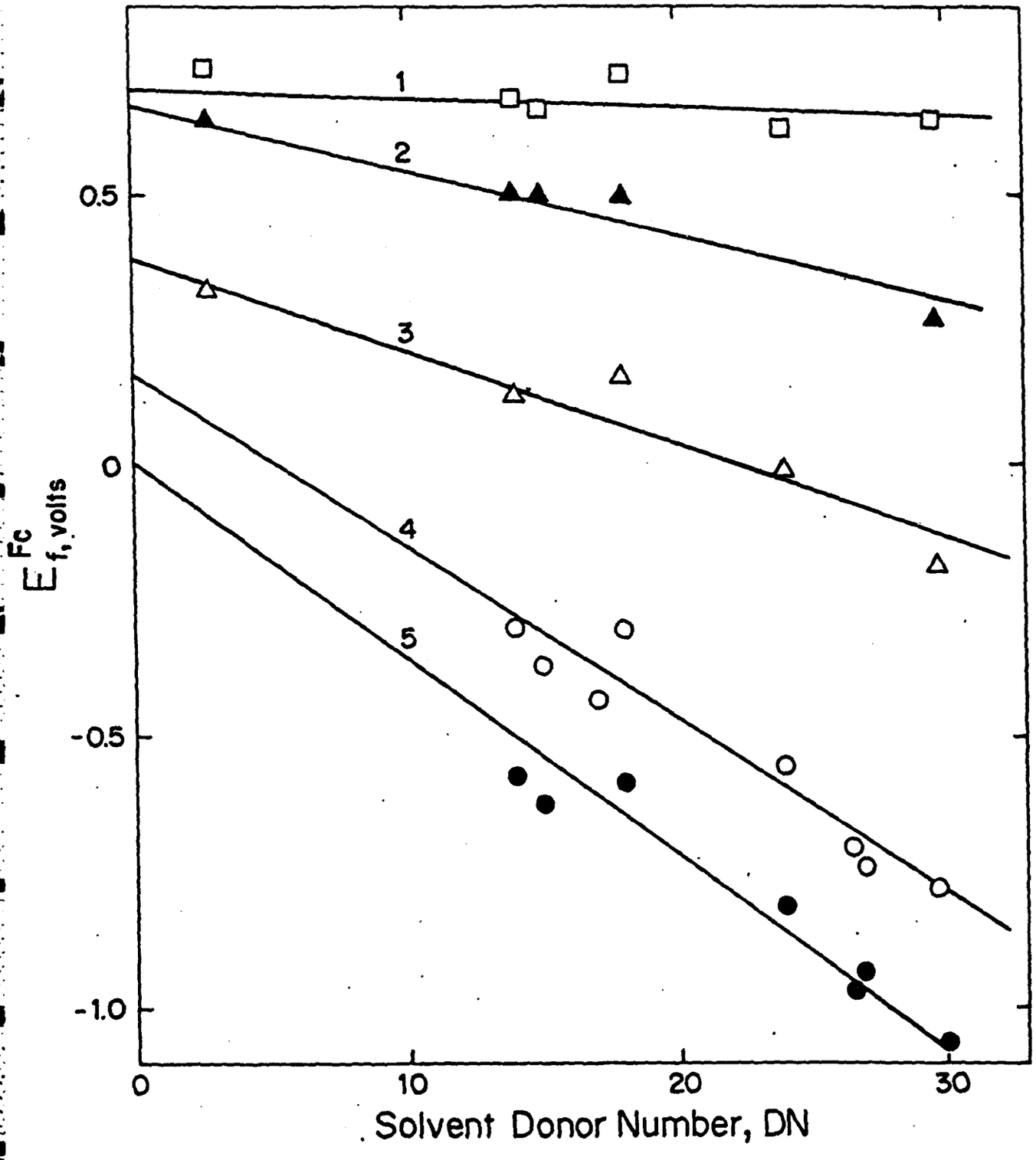

1
2
3
4
5
0.5
0
-0.5
-1.0
$E^{Fc}_{f,\ volts}$
0
10
20
30
Solvent Donor Number, DN

FIGURE CAPTIONS

Figure 1

Schematic plots outlining outer-shell free energy-reaction coordinate profiles for redox couple $O + e^- \rightleftharpoons R$ on the basis of the hypothetical two-step charging process, as outlined in the text. (A) Y-axis: ionic free energy; (B) Y-axis: electrochemical free energy (i.e., including energy of reacting electron). The pathways OT'S' and OTS, marked by arrows, represent hypothetical two-step charging process, starting from the stable oxidized form, by which the nonequilibrium free-energy profile OT'T corresponding to the thermal activation process can be deduced. T is the transition state since this forms the intersection point of the two nonequilibrium free-energy curves starting from the oxidized and reduced forms, OT and RT, respectively.

Figure 2

Schematic outer-shell free energy-reaction coordinate plots outlining influence of specific reactant-solvent interactions upon "static" component of outer-shell barrier. (A) Profile expected from the continuum model [Eq. (3)]; (B) Profile anticipated in presence of specific reactant-solvent interactions, with stronger interactions for oxidized (O) relative to reduced (R) species.

Figure 3

"Donor Selectivity" plots of formal potential of redox couple versus ferricinium-ferrocene in given solvent, E_f^{Fc}, against solvent Donor Number DN. DN values taken from V. Gutmann, "Donor-Acceptor Approach to Molecular Interactions", Plenum, New York, 1978, Chapter 2. Key: (1) $Fe(bpy)_3^{3+/2+}$ (bpy = 2,2'-bipyridine), (2) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, (3) $Ru(NH_3)_4bpy^{3+/2+}$, (4) $Ru(NH_3)_6^{3+/2+}$, (5) $Co(en)_3^{3+/2+}$ (en = ethylenediamine). Data for (1), (4), and (5) taken from ref. 22; for (2) and (3), J. T. Hupp, unpublished experiments. Solvents used, in order of increasing donor number (DN values in parentheses): nitromethane (2.7), acetonitrile (14.1), propylene carbonate (15.1), water (18), formamide (24), dimethylformamide (26.6), N-methylformamide (27), dimethylsulfoxide (29.8).

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